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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08K 5/56, 5/59, 5/06		A1	(11) International Publication Number: WO 99/09094 (43) International Publication Date: 25 February 1999 (25.02.99)
(21) International Application Number: PCT/US98/17195 (22) International Filing Date: 21 August 1998 (21.08.98) (30) Priority Data: 60/056,475 21 August 1997 (21.08.97) US 09/137,585 21 August 1998 (21.08.98) US (71) Applicant: HENKEL CORPORATION [US/US]; Suite 200, 2500 Renaissance Boulevard, Gulph Mills, PA 19406 (US). (72) Inventors: NATESH, Anbazhagan; 120 Kent Drive, North Wales, PA 19454 (US). SHAH, Shailesh; 1704 St. Georges Road, Dresher, PA 19025 (US). CONNOR, Michael, P.; 16 Ramsgate Court, Blue Bell, PA 19422 (US). ZANE, William, A.; 3067 Sunny Ayre Drive, Lansdale, PA 19446 (US). BRANDEWIEDE, Louis, J.; 1121 Nash Avenue, Lansdale, PA 19446 (US). LAFREEDA, Ronald, C.; 2434 Butler Pike, Plymouth Meeting, PA 19462 (US). DECKER, Robert, W.; 2771 Narcissa Road, Plymouth Meeting, PA 19462 (US). (74) Agent: MURPHY, Glenn, E., J.; Henkel Corporation, Suite 200, 2500 Renaissance Boulevard, Gulph Mills, PA 19406 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: BETA-HYDROXY MERCAPTANS AS COSTABILIZERS FOR HALOGENATED RESINS			
(57) Abstract The present invention provides a novel combination of stabilizer and costabilizer for inhibiting thermal degradation of halogenated organic resins, resins comprising the stabilizer/costabilizer combination, and methods of stabilizing halogenated organic resins with the combination, wherein the costabilizer is a beta-hydroxymercaptoalkyl ether of the formula $R(CH_2OCH_2CH(OH)CH_2SH)_n$.			

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BETA-HYDROXY MERCAPTANS AS COSTABILIZERS FOR HALOGENATED RESINS

BACKGROUND OF THE INVENTION

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This invention relates to additives for processing halogenated resinous compounds, more particularly to costabilizers that enhance the performance of primary heat stabilizers used to improve the thermal stability of halogenated resins, particularly halogenated vinyl resins, and more particularly, polyvinyl chloride (PVC).

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This invention, as previously noted, relates to additives for the processing of halogenated resins, particularly polyvinyl chloride. In particular, this invention is concerned with enhancing the heat stabilizing performance of primary heat stabilizers used in the processing of halogenated resins. These type resins are known to undergo rapid thermal degradation under the conditions found in the processes to which these resins are subjected, such as, for example, calendaring, extrusion, and injection molding. Thus it has been found necessary to utilize stabilizers in processing halogenated resins to counteract the harmful effects on resin properties of thermal degradation during processing.

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For example, polyvinyl chloride is known to undergo a rapid and sequential elimination of hydrochloric acid, or dehydrochlorination, at elevated process temperatures. Other halogenated resins are known to undergo similar dehydrohalogenation reactions. Dehydrochlorination in PVC can initiate at labile chlorines usually associated with irregularities in the molecular chain, such as branches or double bonds. Once free, the hydrochloric acid further degrades the polyvinyl chloride and can greatly accelerate the rate of degradation through autocatalytic unzipping of the chlorines along the polymer chain. The primary function of heat stabilizers in PVC is to scavenge the free hydrochloric acid and to depress further hydrochloric acid elimination.

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Thus a variety of stabilizing additives have been developed to counteract the thermal degradation of halogenated organic resins. Lead salt stabilizers are widely used

for PVC, but are of increasingly limited applicability because of handling and toxicity concerns. They are also unusable in applications requiring transparency. Mixed metal carboxylate soaps of barium, cadmium, calcium, and zinc are also known, but the resulting chlorides are Lewis acids that further encourage degradation, requiring the use of costabilizers such as epoxidized oils, polyols, and organic phosphites. Barium-cadmium, barium-zinc, and calcium-zinc stabilizers also are known, though cadmium compounds are under increasing scrutiny for toxicological and cost considerations. These latter stabilizers also give rise to compatibility problems when used in higher concentrations and contribute to poor water and heat resistance in the resins.

The use of sulfur-containing organotin or organoantimony compounds as heat stabilizers for halogenated resins is well known. These compounds react with the released halogen acid and are converted into the corresponding metal salts. Although these compounds are very effective stabilizers, they unfortunately have the disadvantage of being the most expensive. In addition, these known organometallic stabilizers do not always satisfy the requirements of applications relating to shelf-life, odor, processing properties, and heat resistance. It would be of significance, therefore, to provide materials that can extend the performance of these stabilizers without compromising resin performance or quality, preferably in fact improving resin performance and quality by their use.

Typical costabilizers known to the art for enhancing the performance of organometallic primary heat stabilizers are sulfur-containing organic ligands having ester functionality. While these known costabilizers can provide excellent heat stability to halogenated organic resins, they typically offer poor resistance to light degradation and poor water resistance due to the ester chemistry. In addition, these costabilizers contribute to odor problems. Thus there remains a need for new, effective costabilizers for halogenated organic resins that avoid the drawbacks associated with the known costabilizers.

It has now been discovered that certain beta-hydroxy mercaptans unexpectedly improve the performance of primary stabilizers, particularly sulfur-containing organotin

and sulfur-containing organoantimony compounds, in the heat stabilization of halogenated resins. The combination provides a stabilizer system which permits more efficient use of primary stabilizers, thus offering resin formulators excellent stabilization at a substantially reduced cost. The combination according to the invention also unexpectedly improves the processing properties of the resins, further providing cost and efficiency improvements to resin processors. The inventive combination also reduces odor problems associated with the processing of resins stabilized thereby and provides increased resistance to resin yellowing associated with thermal degradation.

DESCRIPTION OF THE INVENTION

The present invention relates to a novel combination of beta-hydroxy mercaptan costabilizers and primary heat stabilizers for halogenated organic resins, halogenated organic resins containing the novel combination of mercaptan costabilizers and primary stabilizers, and methods of stabilizing halogenated organic resins with the novel combination of primary stabilizers and beta-hydroxymercaptan costabilizers. The novel combination unexpectedly improves the performance of the primary stabilizers and provides unexpected improvement in the processing properties of the halogenated organic resins stabilized thereby.

The beta-hydroxy mercaptan costabilizers of the present invention are compounds of the formula $R(\text{CH}_2\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{SH})_n$, wherein R is H or an alkyl, alkoxy, aryl, aryloxy, cycloaliphatic, or cyclooxyaliphatic group having one to twenty carbon atoms and n is 1, 2, 3, or 4. Preferably R is C_1 to C_{20} alkyl, more preferably a C_6 to C_{17} alkyl group. Particularly preferred as a the costabilizer of the present invention is a 1-mercapto-2-hydroxypropyl ether derived from a C_4 to C_{10} mixed glycidyl ether.

The beta-hydroxy mercaptans according to the invention can be prepared by methods known in the art per se. One method entails reacting an epoxide compound with hydrogen sulfide, usually in an aqueous medium and optionally in the presence of a catalyst such as sodium hydroxide, porous clay, or alumina. In a preferred embodiment

of this method,

a C₁ to C₁₀ mixed fatty alcohol is reacted in the presence of a catalyst with epichlorohydrin to form a C₁ to C₁₀ mixed glycidyl ether. The glycidyl ether is then reacted with hydrogen sulfide in an aqueous medium in the presence of sodium hydroxide catalyst to form the beta-hydroxymercaptoalkyl ether costabilizer.

The primary stabilizer in the invention can be any of the primary stabilizers of the classes mentioned above, including lead salts, mixed metal carboxylate soaps of barium, cadmium, calcium, or zinc, and barium-cadmium, barium-zinc, and calcium-zinc stabilizers. Preferably, the stabilizer is an organometallic compound of the formula R'_xML_{y-x}, wherein R' is C₁ to C₁₇ alkyl, M is a metal having a valence y of 3 or 4, L is a reactive sulfur-containing ligand, and x is less than y and is 1, 2, or 3. Preferably, the metal M is tin or antimony, and the reactive ligand L is selected from the group consisting of alkylthioalkanoate esters and mercaptoalkylalkanoate esters. In a particularly preferred embodiment, L is an isooctylthioglycolate or a 2-mercaptoethylolate group. In another preferred embodiment, the primary stabilizer is selected from the group consisting of dimethyltinbis(2-ethylhexylthioglycolate), methyltintris(2-ethylhexylthioglycolate), and mixtures thereof. In accordance with the invention, the primary stabilizer and the costabilizer are combined in a weight ratio that ranges between about 1:2 and about 2:1, preferably between about 2:3 and 3:2.

Other organometallic primary stabilizers suitable for use in this invention are disclosed and described in U.S. Patent Nos.: 2,641,588; 2,641,596; 2,680,726; 2,684,956; 2,726,254; 2,789,963; 2,809,956; 2,830,067; 2,855,417; 2,870,119; 2,914,506; 2,998,441; 3,021,302; 3,069,447; 3,126,400; 3,293,273; 3,340,285; 3,396,185; 3,399,220; 3,424,717; 3,466,261; 3,478,071; 3,485,794; 3,530,158; 3,764,571; 4,008,201; 4,062,881; 4,115,352; 4,303,578; 4,310,454; 4,336,176; and 4,701,486, the disclosures of which are hereby incorporated by reference.

The resin used in the present invention can be any organic halogenated resin. The term organic halogenated resin as used herein refers to halogen-containing vinyl and

vinylidene polymers or resins in which the halogen is attached directly to the carbon atoms. Preferably, the polymer is a vinyl halide polymer, more particularly a vinyl chloride polymer. Usually, the vinyl chloride polymer is made from monomers consisting of vinyl chloride alone or a mixture of monomers comprising, preferably, at least about 70% by weight based on the total monomer weight of vinyl chloride.

Other halogen-containing polymers which can be stabilized according to this invention include chlorinated polyethylene having 14 to 75%, e.g. 27%, chloride by weight, chlorinated natural and synthetic rubber, rubber hydrochloride, chlorinated polystyrene, polyvinyl chloride, polyvinylidene chloride, polyvinyl bromide, polyvinylidene bromide, polyvinyl fluoride, polyvinylidene fluoride, copolymers of vinyl chloride with 1 to 90%, preferably 1 to 30%, of a copolymerizable monomer material such as, for example, vinyl acetate, vinyl butyrate, vinyl benzoate, vinylidene chloride, diethyl fumarate, diethyl maleate, other alkyl fumarates and maleates, vinyl propionate, methyl acrylate, 2-ethylhexyl acrylate, butyl acrylate and other alkyl acrylates, methyl methacrylate, ethyl methacrylate, butyl methacrylate and other alkyl methacrylates, methyl alpha-chloroacrylate, styrene, trichloroethylene, vinyl ethers such as vinyl ethyl ether, vinyl chloroethyl ether and vinyl phenyl ether, vinyl ketones such as vinyl methyl ketone and vinyl phenyl ketone, 1-fluoro-2-chloroethylene, acrylonitrile, chloroacrylonitrile, allyl acetate, allylidene diacetate, chloroallylidene diacetate, butadiene, butene, butylene, dibutyl maleate, 1,2-dichloroethylene, ethylene, maleic anhydride, propylene, styrene, vinyl isobutyl ether, vinyl laurate, trans-dichloroethane, maleic acid, acrylic acid, fumaric acid, itaconic acid, and N-vinylpyrrolidinone. Typical copolymers include vinyl chloride-vinyl acetate (96:4 sold commercially as VYNW), vinyl chloride-vinyl acetate (87:13), vinyl chloride-vinyl acetate-maleic anhydride (86:13:1), vinyl chloride-vinylidene chloride (95:5); vinyl chloride-diethyl fumarate (95:5), and vinyl chloride-2-ethylhexyl acrylate (80:20).

The stabilizer/costabilizer combination according to the present invention is added to the halogenated resin in an amount of 0.01 to 10 parts by weight, preferably 0.05 to 5 parts by weight, per 100 parts by weight of resin. The stabilizer/costabilizer

combination can be incorporated into the resin by any one of many known methods that provide for uniform distribution of additives throughout resin compositions, such as, for example, admixing in an appropriate mill or mixer.

Depending on the end use, further additives can be added to the halogenated organic resins according to the invention, such as other stabilizers and costabilizers, lubricants, plasticizers, impact modifiers, fillers, pigments, antioxidants, dyes, ultraviolet light absorbing agents, densifying agents and the like. These additives can be added to the resin separately from the stabilizer/costabilizer combination of the present invention, or they can be combined with the stabilizer/costabilizer combination of the invention to form a complete additive package for the halogenated resins.

The invention will be further understood by reference to the following examples which serve to illustrate, but not limit, the invention.

EXAMPLES

Preparation of Beta-Hydroxymercaptan Costabilizer

A pressure reactor was charged with 150 ml of isopropyl alcohol, 6 g of sodium hydroxide catalyst in the form of a 49.7% aqueous solution, and 30 ml of deionized water. The reactor contents were then saturated with hydrogen sulfide at a pressure of 35 psi. Following saturation with hydrogen sulfide, the reactor was charged over approximately three hours with 315 g of a C₁ to C₁₀ mixed glycidyl ether, commercially available from CVC Specialty Chemicals, Cherry Hill, NJ, as Erisys GE-7, dissolved in isopropyl alcohol. The resulting mixture was allowed to react for approximately two hours at just under 30°C. Following reaction, the vessel was evacuated of hydrogen sulfide using pressurized nitrogen. The reaction mixture was then adjusted to pH 1-3 with concentrated sulfuric acid and stripped of volatiles under vacuum using a nitrogen sparge. After settling overnight, the contents of the reactor were removed to a separatory funnel and filtered, yielding 284 g of 1-mercapto-2-hydroxypropyl C₁ to C₁₀ mixed alkyl

ether, having a viscosity of 25 cps (Brookfield DVLT, #2 spindle), Gardner color <1, and SH value of 3.51 meq/g.

Evaluation of Beta-Hydroxy Mercaptan As Co-Stabilizer

Powdered resin compositions were prepared in accordance with the formulations given in the table below. The quantities are expressed in parts by weight.

Components	Formulation 1	Formulation 2
PVC (Note 1)	100	100
Stabilizer (Note 2)	1.2	1.2
Impact Modifier (Note 3)	8.5	5.5
Lubricant (Note 4)	1	1
Co-stabilizer (control) (Note 5)	0.8	0
Beta-hydroxy mercaptan	0	0.8
Pigment (Note 6)	9	9
Filler (Note 7)	5	5
Paraffin Wax (Note 8)	0.6	0.6
Process Aid (Note 9)	0.5	0.5
Wax (Note 10)	0.15	0.15

Notes:

1. Oxy 225 S.G., polyvinyl chloride available from Occidental Chemical
2. ADVASTAB® TM-181, dimethyltinbis (2-ethylhexylthioglycolate) / methyltintris (2-ethylhexylthioglycolate) stabilizer available from Morton International
3. KM 390, available from Rohn & Haas
4. Loxiol VGE 1883, lubricant available from Henkel Corp., Ambler, PA
5. Stabiol 1079, stabilizer available from Henkel Corp., Ambler, PA
6. R-101, titanium dioxide available from DuPont
7. UFT, stearic-coated calcium carbonate available from Omya
8. Loxiol HOB-7169, available from Henkel Corp., Ambler, PA
9. Ca-St 12b, calcium stearate available from Ferro Corp.
10. AC-629A, oxidized polyethylene wax available from Allied-Signal

Fusion Test

65 g each of the above resin formulations were subjected to fusion testing using a Brabender Plasticorder PL2000 with a number 6 roller head with roller blades at 185°C and 60 rpm. The resin according to the present invention demonstrated no significant difference in fusion time or equilibrium temperature, while providing improved processability due to the decrease in fusion and equilibrium torques.

Property	Formulation 1	Formulation 2
Fusion Time (sec)	50	52
Fus. Torque (mg)	3490	3327
Eq. Torque (mg)	2709	2602
Eq. Temp (°C)	199	198

Stability Test

65 g each of the above resin formulations were subjected to dynamic thermal stability testing using a Brabender Plasticorder PLV300 at 200°C and 60 rpm. The resin formulation according to the invention demonstrated no significant difference in thermal stability, while offering improved processability as evidenced by the lower equilibrium torque.

Property	Formulation 1	Formulation 2
DTS (min)	21	20
Eq. Torque (mg)	1700	1625

Extrusion Test

Samples of each of the above resins were extruded using a Brabender Plasticorder PL2000 fitted with a conical twin screw extruder and a 4" adjustable sheet die. The resins were extruded at 15 rpm through four zones each at 185°C. The formulation according to the invention demonstrated unexpected and significant processing advantages. Torque

was reduced by more than 13% and pressure by more than 18% with no significant changes in resin quality. Moreover, the resin of the invention experienced greatly superior resistance to yellowing (Color b* below).

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Property	Formulation 1	Formulation 2
Avg. Torque (mg)	11443	9914
Avg. P l (psi)	1719	1404
Color L*	96	94.8
Color a*	-0.7	-0.8
Color b*	1.6	1
Gloss 60°	28	26.7
Gloss 85°	79.3	82.9

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THE INVENTION CLAIMED:

1. A composition of matter comprising a combination of (a) a primary stabilizer for inhibiting thermal degradation of a halogenated organic resin and (b) a beta-hydroxymercaptoalkyl ether of the formula $R(CH_2OCH_2CH(OH)CH_2SH)_n$, wherein R is H or an alkyl, alkoxy, aryl, aryloxy, cycloaliphatic, or cyclooxyaliphatic group having one to twenty carbon atoms and n is 1, 2, 3, or 4, said combination having a weight ratio of (a) to (b) ranging between about 1:2 and about 2:1.

2. A composition according to claim 1, wherein R is a C_6 to C_{12} alkyl group.

3. A composition according to claim 2, wherein the ratio of (a) to (b) ranges between about 2:3 and about 3:2.

4. A composition according to claim 3, wherein the primary stabilizer is an organometallic compound of the formula $R'ML_x$, wherein R' is C_1 to C_{12} alkyl, M is a metal having a valence y of 3 or 4, L is a reactive sulfur-containing ligand, and x is less than y and is 1, 2, or 3.

5. A composition according to claim 4, wherein M is tin or antimony and L is selected from the group consisting of alkylthioalkanoate esters and mercaptoalkylalkanoate esters.

6. A composition according to claim 5, wherein L is selected from the group consisting of isooctylthioglycolate and 2-mercaptoethyloleate.

7. A composition comprising a halogenated organic resin and a stabilizing effective amount of a combination of (a) a primary stabilizer for inhibiting thermal degradation of a halogenated organic resin and (b) a beta-hydroxymercaptoalkyl ether of the formula $R(CH_2OCH_2CH(OH)CH_2SH)_n$, wherein R is H or an alkyl, alkoxy, aryl, aryloxy, cycloaliphatic, or cyclooxyaliphatic group having one to twenty carbon atoms and n is 1, 2, 3, or 4, said combination having a weight ratio of (a) to (b) ranging between

about 1:2 and about 2:1.

8. A composition according to claim 7, wherein the halogenated organic resin is selected from the group consisting of halogen-containing vinyl and vinylidene resins.

9. A composition according to claim 8, wherein the resin comprises at least 70% by weight vinyl chloride or vinylidene chloride units.

10. A composition according to claim 9, wherein the primary stabilizer is an organometallic compound of the formula R'_yML_x , wherein R' is C_1 to C_{12} alkyl, M is a metal having a valence y of 3 or 4, L is a reactive sulfur-containing ligand, and x is less than y and is 1, 2, or 3.

11. A composition according to claim 10, wherein M is tin or antimony and L is selected from the group consisting of alkylthioalkanoate esters and mercaptoalkylalkanoate esters.

12. A composition according to claim 11, wherein L is selected from the group consisting of isooctylthioglycolate and 2-mercaptoethylolate.

13. A composition according to claim 10, wherein the combination of (a) and (b) is dispersed in the resin in an amount ranging from about 0.01 to about 10 parts of said combination in each 100 parts of the resin.

14. A method of stabilizing a halogenated organic resin against thermal degradation comprising adding to the resin a stabilizing effective amount of a combination of (a) a primary stabilizer for inhibiting thermal degradation of a halogenated organic resin and (b) a beta-hydroxymercaptoalkyl ether of the formula $R(CH_2OCH_2CH(OH)CH_2SH)_n$, wherein R is H or an alkyl, alkoxy, aryl, aryloxy, cycloaliphatic, or cyclooxyaliphatic group having one to twenty carbon atoms and n is

1, 2, 3, or 4, said combination having a weight ratio of (a) to (b) ranging between about 1:2 and about 2:1.

15. A method according to claim 14, wherein the primary stabilizer is an organometallic compound of the formula R'_xML_x , wherein R' is C₁ to C₁₂ alkyl, M is a metal having a valence y of 3 or 4, L is a reactive sulfur-containing ligand, and x is less than y and is 1, 2, or 3.

16. A method according to claim 15, wherein M is tin or antimony and L is selected from the group consisting of alkylthioalkanoate esters and mercaptoalkylalkanoate esters.

17. A method according to claim 16, wherein L is selected from the group consisting of isooctylthioglycolate and 2-mercaptoethyloleate.

18. A method according to claim 17, wherein the combination of (a) and (b) is added to the resin in an amount ranging from about 0.01 to about 10 parts of said combination in each 100 parts of the resin.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/17195

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08K 5/56, 5/59, 5/06

US CL : 252/400.1, 406; 524/177, 178, 179, 180, 367, 368

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/400.1, 406; 524/177, 178, 179, 180, 367, 368

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2,641,588 A (LEISTNER ET AL) 09 June 1953 (09-06-53), column 1, line 1 through column 3, line 36.	1-16
Y	US 2,726,254 A (LEISTNER ET AL) 06 December 1955 (06-12-55), column 1, line 1 through column 2, line 26.	1-16
Y	US 2,809,956 A (MACK ET AL) 15 October 1957 (15-10-57), column 1, line 1 through column 2, line 31.	1-16
Y	US 2,914,506 A (MACK ET AL) 24 November 1959 (24-11-59), column 1, line 15 through column 5, line 19.	1-16
Y	US 3,293,273 A (GLOSKEY) 20 December 1966 (20-12-66), column 1, line 9 through column 4, line 54.	1-16

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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01 DECEMBER 1998

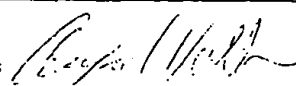
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Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

Kriellion Sanders 
Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/17195

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,340,285 A (REMES ET AL) 05 September 1967 (05-09-67), column 1, line 11 through column 4, line 71.	1-16
Y	US 4,290,942 A (SCHNEIDER ET AL) 22 September 1981 (22-09-81), column 1, line 10 through column 2, line 51	1-16
Y	US 4,303,578 A (MICHAELIS) 01 December 1981 (01-12-81), see the abstract.	1-16
Y	US 4,357,434 A (MIYOSHI ET AL) 02 November 1982 (02-11-82), see the abstract.	1-16